

Theoretical investigation of local motion and establishment of displacive properties with order disorder ferroelectric properties in NaNO_2 molecule on basis of NMR data

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Abstract

After discovery of ferroelectric properties of NaNO_2 , it was classified as order disorder type ferroelectric material based on earlier studies. Along with this and result carried out from our recent theoretical analysis of electric field gradients due to quadrupolar nucleus ^{23}Na in this crystal clearly indicate the presence of another type of local motion with reorientation of NO_2 groups during polarization reversal. It is the displacement of Na atom in crystalline space with considerable amount. For this we have obtained ratios; $M_{1111}/M_{3333} = 0.71$, $M_{1133}/M_{3333} = -0.74$, $M_{2323}/M_{3333} = 0.07$, $M_{3131}/M_{3333} = 0.17$, $M_{1212}/M_{3333} = 0.17$ of M-tensor components by using point charge model. Their values are found for flipping angle 172° w.r.t. direction specified by direction cosines $l_1 = 0.996$, $l_2 = 0.075$, $l_3 = 0.0486$ of NO_2 groups and displacement of Na atom in c -, a -, b -crystalline space $d_c = 0.015$ nm, $d_a = -0.046$ nm, $d_b = 0.048$ nm. Values of these ratios of M-tensor components are found in very good agreement with NMR experimental values of MTR's measured by earlier researchers. For these theoretical values of M-tensor ratios, we have found minimum value of sum of square deviation $S (=0.0070)$. This analysis confirmed the possibility of displacive nature with order disorder nature of NaNO_2 ferroelectric material. A study based on XRD analysis of NaNO_2 by M. Ichikawa et al. (2002) also confirmed that the ferroelectric transition of NaNO_2 is not of pure order-disorder type.

Keywords

M-tensor ratios (MTR), quadrupolar nuclei, electric field gradients (e.f.g.'s), sum of square deviation, displacive ferroelectric, order disorder ferroelectrics

1. Introduction

Sodium nitrite is a ferroelectric material [1] which undergoes an order-disorder transition, first to a sinusoidal antiferroelectric phase at 437 K and then to a paraelec-

tric phase at 438 K [2, 3]). At low temperatures, the NO_2 groups are believed to be aligned in the bcc plane of the orthorhombic unit cell [4], shown in Fig. 1a, with their electric dipole moments pointing along one direction of the ferroelectric b -axis. The transition from the ferroelec-

tric phase occurs by progressive reversal of the orientations of the NO_2 groups, so that, in the paraelectric phase, their dipole moments are oriented with equal probability along the two directions of the b -axis [5, 6]. The ferroelectric-paraelectric phase transition takes place at about 437 K, where the high temperature phase is centrosymmetrical in body centered orthorhombic system with the space group $D_{2h}^{25} - Immm$, with the dipoles disordered with respect to the b -axis, in a narrow temperature range from 435.5 to 437 K, there exists an incommensurate and ferroelectric phase. The melting temperature is 550 K. Different from displacive ferroelectrics in which the ferroelectric transition is driven by soft phonon modes, NaNO_2 offers order-disorder structural phase transition and any associated ferroelectric instability [1, 7, 8].

The crystal structure of NaNO_2 was accurately determined by [4, 9]. As shown in Fig. 1, the unit cell has two molecules with the same point symmetry. The lattice belongs to the non-centrosymmetrical body centered orthorhombic system with the space groups $C_{2v}^{20} - Im2m$. The dimensions of the cell are $a = 0.3560 + 0.0010$ nm, $b = 0.5560 + 0.0005$ nm, and $c = 0.5384 + 0.0005$ nm at room temperature. The position of atoms in the unit cell is [9],

2N	(0, 0, 0; 1/2, 1/2, 1/2)	+	(0, t , 0)
2Na		+	(0, w , 0)
4O		+	(0, u , v ; 0, u , $-v$)

The values of the atomic co-ordinates as fraction of unit cell dimensions are $t = 0.1200 + 0.0007$, $w = 0.5853 + 0.0010$, $u = 0.0000$ and $v = 0.1941 + 0.0006$ at room temperature.

The spin-lattice relaxation of nuclei with $I > 1/2$ in non-metallic crystalline solids of high purity is usually dominated by the interaction of the nuclear electric quadrupole moment with thermal fluctuations in the electric

field gradient [10–12]. For $I = 3/2$ nuclei, such as ^{23}Na , the allowed quadrupole transitions are $m = \pm 3/2 \rightarrow \pm 1/2$ ($\Delta m = \pm 1$) with a probability denoted by W_1 , and $m = \pm 3/2 \rightarrow m/2$ ($\Delta m = \pm 2$) with a probability denoted by W_2 . These probabilities are of the same order of magnitude but have a different dependence on the orientation of the crystal relative to a strong external magnetic field [13]. If the nuclei are situated at identical sites in a single crystal, the relaxation is homogeneous and described by the components of a fourth-rank tensor, the so-called M-tensor [14].

Extensive experimental work on NaNO_2 has been devoted in probing the mechanism of the NO_2 polarization reversal that triggers the order-disorder transition. Most studies support the c axis rotation model, but there were also results favoring the a -axis rotation model [15]. Recently, refined X-ray studies over a wide temperature range reinforced the c -axis rotation model [15, 16]. On the theoretical side, the microscopic model calculations done by K.D. Ehrhardt and K.H. Michel supported the c -axis rotation mechanism [17], whereas mixed double rotations around the a -axis and the c -axis was suggested by W. Kinase and K. Takahashi [18].

D.G. Hughes and P.A. Spencer [19] theoretically estimated the value of M-tensor ratios for Na in NaNO_2 by assuming that the relaxation is entirely caused by individual NO_2 groups which are suddenly reorienting (reversing their orientation) in the bc -plane, the agreement between the two sets of experimental data at temperature 432 and 448 K and the theoretical estimate is probably as good as could be expected, except in the case of the ratio M_{1212}/M_{3333} shows large deference from its experimental value implies either that the NO_2 groups do not rotate through exactly 180° , or that the axis of rotation is not parallel to the a -axis. In either case, this may be because of the presence of other nearby disordered NO_2 groups.

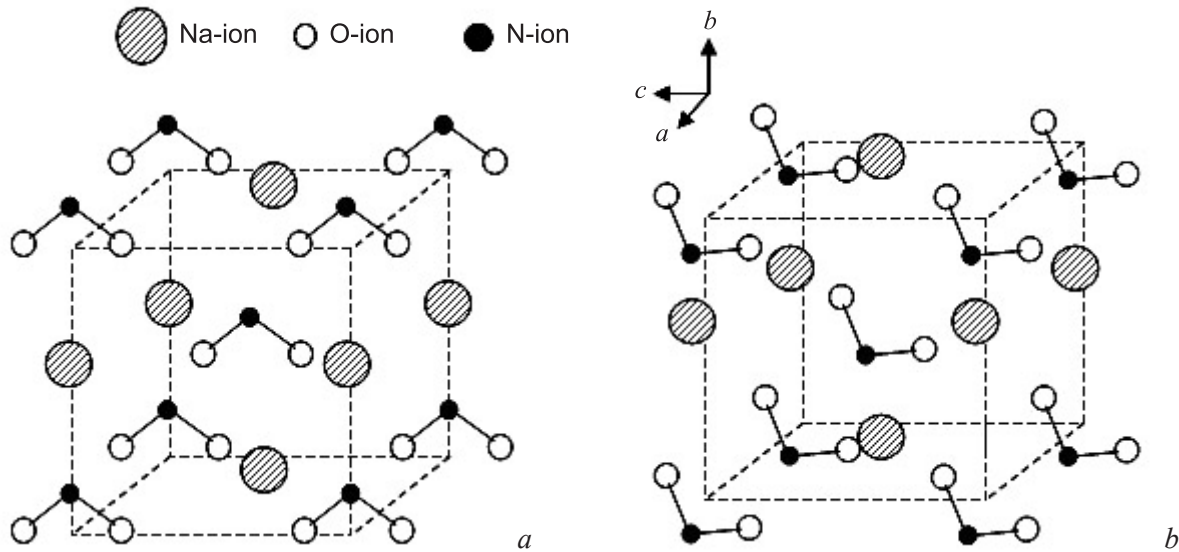


Figure 1. Unit cell of NaNO_2 (a) in ferroelectric phase [4, 9, 19, 20] and (b) in antiferroelectric phase after θ angle flipping on NO_2 groups with respect to a direction specified by direction cosine l_1, l_2, l_3 in space and taking Na-ion displacement from old position to new position by d_a, d_b, d_c along a -, b -, c -crystalline directions

M. Kotecha and L. Pandey [20] shows that the small displacement of ‘Na’ atom plays the most important role to explain the spin-lattice relaxation in NaNO_2 with polarization reversal mechanism due to reorientation of NO_2 groups. They obtained the best represented theoretical data of M-tensor ratios by using point charge model for experimental data but the ratios M_{1111}/M_{3333} differ significantly. Y. Dai et al. [21] reported that NO_2^- ions in NaNO_2 crystals exhibit a two-fold rotational motion around the crystallographic b -axis, with an activation energy of about 68 ± 5 kJ/mol. Using solid-state ^{17}O NMR spectroscopy, they effectively demonstrated how NMR techniques can be used to study ion dynamics in solid-state systems. J.P. Dürholt and R. Schmid [22] explored the ferroelectric–paraelectric phase transition in NaNO_2 through *ab initio* molecular dynamics. Their study suggests that the transition shows a combination of displacive and order–disorder characteristics, with polarization reversal primarily driven by the rotation of nitrite ions along the c -axis. Hence from the discovery of ferroelectric properties in NaNO_2 actual internal dynamical motions of ions in NaNO_2 during phase transition was clearly not understood until now.

Apart from these previous works, in this paper we have established the concept of displacive nature of Na atom

$$H_Q = \frac{eQ}{4I(2I-1)} \left[V_0 (3I_z^2 - I^2) + V_+ (I^- I_z + I_z I^-) + V_- (I^+ I_z + I_z I^+) + V_{+2} (I^-)^2 + V_{-2} (I^+)^2 \right] \quad (1)$$

Where $V_0 = V_{zz}$, $V_{\pm} = V_{zx} \pm iV_{zy}$, and $V_{\pm 2} = 1/2(V_{xx} - V_{yy}) \pm iV_{xy}$ are the combinations of electric field gradients components represented by second rank symmetric tensor $V_{\alpha\beta}$ and $I^+ = I_x + iI_y$ and $I^- = I_x - iI_y$ are the raising and lowering operator. eQ is the quadrupole moment of quadrupolar nuclei. Eq. (1) gives the form of the quadrupole coupling that is particularly useful for considering relaxation in which the principal axes are not fixed in space but rather are function of time.

For NaNO_2 molecule ^{23}Na atom ($I = 3/2$) charge distribution not symmetric in spherical manner hence if any local motion takes place by nearest NO_2 groups then it interacts with external charge distribution, consequently e.f.g.’s at nuclear site has change. Transition probabilities W_1 ($\pm 3/2 \rightarrow \pm 1/2$) and W_2 ($\pm 3/2 \rightarrow m1/2$), which are strongly orientation dependent and temperature dependent [13, 14, 24–27], are represented in terms of “e.f.g.’s multiples” (generally known as M-tensor components). Equation (1) is re-written by using matrix notation for nuclei ($I = 3/2$)

$$\begin{bmatrix} \frac{e^2 qQ}{4} & \frac{eQ}{2\sqrt{3}}(V_{zx} - iV_{zy}) & \frac{eQ}{2\sqrt{3}}\left(\frac{1}{2}hV_{zz} - iV_{xy}\right) & 0 \\ \frac{eQ}{2\sqrt{3}}(V_{zx} - iV_{zy}) & -\frac{e^2 qQ}{4} & 0 & \frac{eQ}{2\sqrt{3}}\left(\frac{1}{2}hV_{zz} - iV_{xy}\right) \\ \frac{eQ}{2\sqrt{3}}\left(\frac{1}{2}hV_{zz} - iV_{xy}\right) & 0 & -\frac{e^2 qQ}{4} & -\frac{eQ}{2\sqrt{3}}(V_{zx} - iV_{zy}) \\ 0 & \frac{eQ}{2\sqrt{3}}\left(\frac{1}{2}hV_{zz} - iV_{xy}\right) & -\frac{eQ}{2\sqrt{3}}(V_{zx} - iV_{zy}) & \frac{e^2 qQ}{4} \end{bmatrix} \quad (2)$$

in NaNO_2 along with polarization reversal mechanism due to reorientation of NO_2 groups. Our analysis clearly nearly supports, c -axis rotation model for NO_2 groups during polarization reversal mechanism. Basic theme of our present work is to explain the actual real dynamical local motions in NaNO_2 based on nuclear magnetic resonance (NMR) experimental M-tensor data and comparing these with theoretical M-tensor data obtained by using point charge model.

2. Theory for orientation dependence of W_1 and W_2 quadrupolar transition probabilities

For quadrupolar nuclei quadrupole perturbation Hamiltonian is given by [23]

From this matrix Eq. (2) it is clear that the $I = 3/2$ and $-3/2$ energy levels are shifted toward higher energy state with an equal shift of $e^2 qQ/4$ and $I = 1/2$ and $-1/2$ energy levels are shifted toward lower energy state with an equal shift of $e^2 qQ/4$ by quadrupole interaction of ^{23}Na nuclei with sudden change of external charge distribution which arises from flipping motion of NO_2 groups and displacive motion of Na atom in NaNO_2 . The quadrupolar perturbed Hamiltonian for transition $m = \pm 3/2 \rightarrow \pm 1/2$ (W_1) and $m = \pm 3/2 \rightarrow m1/2$ (W_2) are given as

$$\left\langle \frac{3}{2}, \pm \frac{3}{2} \left| H_Q(t) \right| \frac{3}{2}, \pm \frac{1}{2} \right\rangle = \pm \left(\frac{eQ}{2\sqrt{3}} \right) (V_{zx}(t)mV_{zy}(t)) \quad \left\langle \frac{3}{2}, \pm \frac{3}{2} \left| H_Q(t) \right| \frac{3}{2}, m\frac{1}{2} \right\rangle = \left(\frac{eQ}{2\sqrt{3}} \right) \left(\frac{1}{2}hV_{zz}(t)mV_{xy}(t) \right) \quad (3)$$

Here $V_{zx}(t)$, $V_{zy}(t)$, $V_{zz}(t)$, $V_{xy}(t)$ are random function of time t , thus above matrix elements for quadrupole interaction H_Q are also random functions of time t .

The transition probability W_1 ($m = \pm 3/2 \rightarrow \pm 1/2$) per unit time is given by [27]

$$W_1 = \frac{e^2 Q^2}{12h^2} \int_{-\infty}^{\infty} \left[\overline{V_{zx}(t) + iV_{zy}(t)} \right] \times \left[V_{zx}(t+\tau) - iV_{zy}(t+\tau) \right] e^{-i\omega_1 \tau} d\tau. \quad (4)$$

And, transitions probability W_2 ($m = \pm 3/2 \rightarrow m1/2$) is given by,

$$W_2 = \frac{e^2 Q^2}{48h^2} \int_{-\infty}^{\infty} \left[\overline{(\eta(t)V_{zz}(t) + 2iV_{xy}(t))} \right] \times \left[(\eta(t+\tau)V_{zz}(t+\tau) + 2iV_{xy}(t+\tau)) \right] e^{-i\omega_2 \tau} d\tau. \quad (5)$$

The expression

$$\frac{1}{h^2} \int_{-\infty}^{\infty} \left[\overline{V_{zx}(t) + iV_{zy}(t)} \right] \times \left[V_{zx}(t+\tau) - iV_{zy}(t+\tau) \right] e^{-i\omega_1 \tau} d\tau,$$

used in Eq. (4) can be converted into real fourth rank tensor form that is well known M-tensor [14, 28], its components $M_{\alpha\beta\alpha'\beta'}$ where $\alpha, \beta, \alpha', \beta' = 1, 2$ and 3 represented as x - y -, z -axes of crystalline co-ordinate system contained information about the dynamical environment of spin system [14, 20, 24]. These M-tensor components are given by [20, 24],

$$M_{\alpha\beta\alpha'\beta'} = \frac{2\pi}{h} \sum_{n,n'} \exp\left(-\frac{E_n}{kT}\right) \langle n' | f_{\alpha\beta} | n \rangle \times \langle n' | f_{\alpha'\beta'}^* | n \rangle \delta(E_n - E_{n'} + E_{m+\mu} - E_m) \times \left(\sum_{n,n'} \exp\left(-\frac{E_n}{kT}\right) \right)^{-1}. \quad (6)$$

Where E_n and E_m are Eigen values of the lattice and spin system, n and n' are initial and final lattice states and μ is 1 and 2 for W_1 and W_2 transitions respectively [20]. Here the product of dynamical quantities

$$\langle n' | f_{\alpha\beta} | n \rangle \text{ and } \langle n' | f_{\alpha'\beta'}^* | n \rangle \text{ is given by,} \\ \langle n' | f_{\alpha\beta} | n \rangle \langle n' | f_{\alpha'\beta'}^* | n \rangle = (\delta V_{zx})^2 + (\delta V_{zy})^2. \quad (7)$$

In Eq. (6) the quantity

$$\frac{\exp\left(-\frac{E_n}{kT}\right)}{\sum_{n,n'} \exp\left(-\frac{E_n}{kT}\right)} = P, \quad (8)$$

represent the probability of lattice having n -state at time t , which is equal for all atom in six nearest NO_2 groups to ^{23}Na atom in NaNO_2 ferroelectric molecule, here we as-

sume NO_2 assembly as a rigid rotator because there is not any relative shifting motion is considered, as predicted by many workers [27]. For the calculation of theoretical values of M-tensor ratios we considered six nearest NO_2 groups to ^{23}Na atom because the M-tensor components vary as r^{-6} , again from the law of energy conservation initial total energy (spin + lattice) of system is equal to final state total energy, i.e., transition $n \leftrightarrow n'$ and $m + \mu \leftrightarrow m$ occurs during phase transition (ferroelectric $\leftrightarrow$ antiferroelectric) in quadrupolar nuclei ($I > 1/2$) only when following condition is fulfilled.

$$E_n + E_m = E_{n'} + E_{m+\mu}. \quad (9)$$

In this case $\delta(E_n - E_{n'} + E_{m+\mu} - E_m) = 1$ from the δ -function properties. Thus, for non-zero value of W_1 can be written, by using Eq. (4)–(7) and (9)

$$W_1 = \frac{2\pi e^2 Q^2 P}{12h} \sum_{n,n'} \left[(\delta V_{zx})^2 + (\delta V_{zy})^2 \right]. \quad (10)$$

In Eq. (10), δV_{zx} and δV_{zy} are independent of time and dependence of orientation of static magnetic field H_0 w.r.t. crystalline frame of reference whose z -axis taking along b -direction two-fold rotational symmetry and its xy plane are the c (- a) plane. The orientation of H_0 w.r.t. crystalline frame is defined by polar and azimuthal angles θ and ϕ respectively [24]. Hence let us denote in general these changes of e.f.g.'s as linear combination of changes of e.f.g.'s in crystalline frames of reference xyz .

$$\delta V_{\alpha\beta}(x, y, z) = \sum_{\alpha\beta} C(\theta, \phi) \delta V'_{\alpha\beta}(x', y', z'). \quad (11)$$

Here coefficients C are the functions of polar and azimuthal angles θ and ϕ , $x'y'z'$ is the coordinate system whose z' -axis coincide with H_0 .

On applying Eq. (11) in Eq. (10) we obtain

$$W_1 = \frac{e^2 Q^2}{12} \left[\sum_{\alpha\beta\alpha'\beta'}^{3333} C_{\alpha\beta\alpha'\beta'}(\theta, \phi) M_{\alpha\beta\alpha'\beta'}(x', y', z') \right]. \quad (12)$$

Where $M_{\alpha\beta\alpha'\beta'}(x', y', z') = (2\pi/h) P \delta V'_{\alpha\beta} \delta V'_{\alpha'\beta'}$ are the M-tensor components in terms of $x'y'z'$ co-ordinate system, which are evaluated by applying simple point charge model considering various local motions of atom in lattice. Similarly, we can obtain the expression for W_2

$$W_2 = \frac{e^2 Q^2}{48} \left[\sum_{\alpha\beta\alpha'\beta'}^{3333} D_{\alpha\beta\alpha'\beta'}(\theta, \phi) M_{\alpha\beta\alpha'\beta'}(x', y', z') \right]. \quad (13)$$

Eqs. (12) and (13) shows the orientation dependence of W_1 and W_2 . Transition probability and the general expressions for this were derived by R.E. Synder and D.G. Hughes [24].

Similar to previous researchers [19], we choose the x - and y -axes to coincide with the c - and a -axes respectively of the unit cell as shown in Fig. 1. Our coordinate system is therefore the same as that previously used to describe

the time-averaged electric field gradient at the ^{23}Na sites at room temperature [29, 30].

Experimental determination of W_1 (or W_2) as a function of orientation of the external field w.r.t. the principal axis system directly yields the values of $M_{\alpha\beta\alpha'\beta'}$. D.G. Hughes and coworkers [13, 19, 24] have done considerable amount of work on this and they obtained values of M-tensor components obtained by experimentally by measuring the orientation dependence of W_1 . The experimental values of M-tensor ratios are given in Table 2, at temperature of our interest [19].

3. Values of $M_{\alpha\beta\alpha'\beta'}$ using point charge model of NO_2

Point charge model is an important tool for the understanding the local motions inside the crystal especially ferroelectric crystals. The ferroelectricity in NaNO_2 arises due to progressive ordering of the permanent electric dipoles associated with the NO_2 groups. Therefore, it is worthwhile to calculate the M-tensor components by obtaining changes in the electric field gradients produced at the ‘Na’ sites due to flipping motions of these dipoles by using point charge model for NO_2 groups and considering displacive motion of Na atom in NaNO_2 . We have considered different possible flipping motions of NO_2 and taking various type of displacements of Na atom in space. In present work, we have focused the displacive motion of Na atom in space with order disorder character of NO_2 .

For the calculations of M-tensor components using point charge model, the NO_2 group was considered as an assembly of three-point charges with charges equal to $-0.562e$ and $+0.124e$ on ‘O’ and ‘N’ respectively [25]. The choice of the values of these charges is consistent with the anti-shielding factor. The electric field gradients were calculated using the expression of potential due to a point charge q at a distance r is expressed by [28]

$$V_{\alpha\beta} = \frac{\partial^2 V}{\partial x_\alpha \partial x_\beta} = \frac{q}{4\pi\epsilon_0 r^3} (3x_\alpha x_\beta - \delta_{\alpha\beta} r^2). \quad (14)$$

Here r is the relative position of atoms of NO_2 assembly from ‘Na’ atom in NaNO_2 . Now from this Eq. (14), we obtain the time average values of e.f.g.’s change due to reorientation of NO_2 groups (here sums run over three-point charges N, O, O in NO_2 assembly) which are given as,

$$\delta V_{\alpha\beta} = \sum_{i=1}^3 \left[(V_{\alpha\beta})_{\text{old}} - (V_{\alpha\beta})_{\text{new}} \right]_i. \quad (15)$$

And from Eq. (6) components of M-tensor due to reorientation of six nearest NO_2 groups to “Na” ion in crystalline xyz co-ordinate system are given as

$$M_{\alpha\beta\alpha'\beta'}(x, y, z) = \frac{2\pi}{h} P \sum_{j=1}^6 (\delta V_{\alpha\beta} \delta V_{\alpha'\beta'})_j. \quad (16)$$

In the case of NaNO_2 we need only six independent M-tensor components M_{1111} , M_{3333} , M_{3131} , M_{2323} and M_{1212} . we can easily obtain these components from Eq. (16), and by using a program written by us in BASIC for evaluating theoretical values of M-tensor ratios taking various values of θ , l_1 , l_2 , l_3 ; d_a , d_b , and d_c .

4. Result and discussion

By using point charge model, we have calculated theoretical values of MTR’s for ^{23}Na in NaNO_2 molecules assuming different type of flipping motion of NO_2 groups (i.e. flipping angle θ and flipping directions cosine l_1 , l_2 , l_3) and taking various value of Na-ion displacements d_c , d_a , d_b along crystalline c -, a -, b -axis.

For theoretical analysis and finding real dynamical motion in NaNO_2 during polarization reversal mechanism, we have considered following possibilities –

- (1) Flipping of NO_2 group’s w.r.t. a -axis proximity with and without taking displacement of Na-atom in crystalline space.
- (2) Flipping of NO_2 group’s w.r.t. c -axis proximity with and without taking displacement of Na-atom in crystalline space.
- (3) Flipping of NO_2 group’s w.r.t. any arbitrary direction (l_1 , l_2 , l_3) in the crystalline space with and without taking displacement of Na-atom.

For first case, we estimated M-tensor ratios for ^{23}Na in NaNO_2 choosing flipping nearest to crystalline a -axis we found that the value of M-tensor ratios obtained from the experimental values for different value of parameters θ ; l_1 , l_2 , l_3 ; d_a , d_b , d_c and testing them for large numbers of set of these parameters, we found that the value of M-tensor ratios did not best match with NMR experimental value of MTR’s [19] (given in Table 2). Same inconsistency with experimental data was found for third case also.

On the other hand, for the second case, we have taken 180° flipping of NO_2 groups about the c -axis without taking any displacive motion of the Na atom, as assumed in a previously widely known fact about ferroelectricity of NaNO_2 . In this case also, calculated M-tensor data are inconsistent with experimental data. Again, we have checked different flipping directions nearest to the c -axis without taking the displacement of the Na-atom, and the same inconsistency was found with the experimental data as in previous case. The above inconsistencies clearly indicate the possibility of other local motions in NaNO_2 with a NO_2 polarization reversal mechanism. Using this concept once more, we have calculated M-tensor ratios, by assuming a displacement of Na atoms in space and sudden reorientation of NO_2 groups along directions whose direction cosines are l_1 , l_2 , l_3 and various flipping angles of NO_2 . Through this consideration, we have obtained theoretical M-tensor ratio data and obtained the sum of square deviation (S) from corresponding experimental data at $T = 298$ K. Figure 2 shows the logarithmic plot

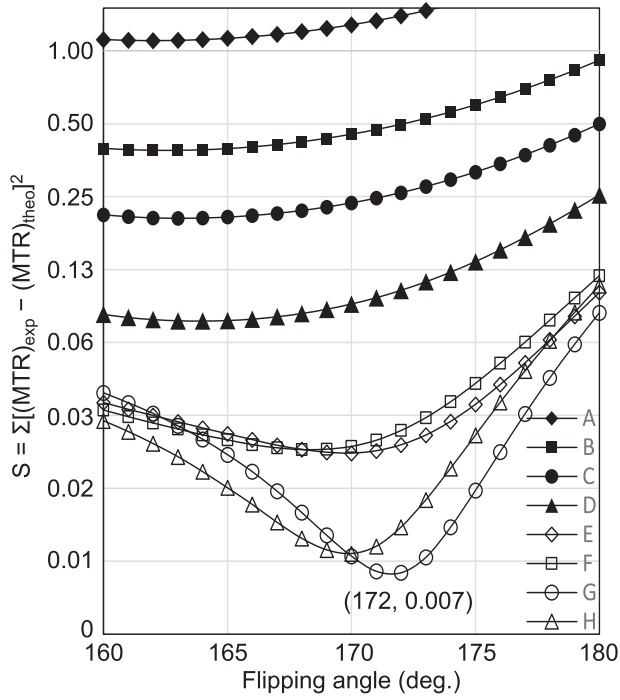


Figure 2. Logarithmic plot sum of square deviation of theoretical M-tensor ratios from NMR experimental M-tensor ratio $S^{\dagger} = \Sigma[(MTR^*)_{\text{exp}} - (MTR)_{\text{theo}}]^2$ for NaNO_2 as a function of flipping angle θ of NO_2 groups at $T = 298$ K (for fixed flipping direction cosines l_1, l_2, l_3 and Na atom displacement from old position co-ordinate (d_a, d_b, d_c) represented in plot by symbol A, B, C, D, E, F, G, H). $^{\dagger}S$ is sum of square deviations of experimental to theoretical M-tensor ratios (MTR^*).

Table 1. Various groups of dependent variables

Groups	Flipping direction cosine			Na atom displacement along crystalline a -, b -, c -axis (in nm)		
	l_1	l_2	l_3	d_c	d_a	d_b
A	0.983	0.150	0.1059	0	-0.025	0.030
B	0.986	0.140	0.0906	0.002	-0.027	0.034
C	0.990	0.110	0.0883	0.004	-0.029	0.036
D	0.992	0.100	0.0770	0.006	-0.034	0.038
E	0.994	0.090	0.0622	0.008	-0.038	0.044
F	0.996	0.045	0.0772	0.010	-0.041	0.046
G	0.996	0.075	0.0486	0.015	-0.046	0.048
H	0.996	0.037	0.0813	0.020	-0.048	0.050

for S as a function of the flipping angle of NO_2 groups for various groups of other parameters $l_1, l_2, l_3, d_c, d_a, d_b$ specified in the plot by the symbols A, B, C, D, E, F, G, H; parameters corresponding to these symbols are shown in Table 1. From the plot, we have obtained minimum value of S , and the best minimum value of S is 0.007 at 172° for the (G) group of data.

In Fig. 3, the M-tensor ratios are represented as a function of b -, a -, and c -axis displacement for fixed values of other parameters (taking $\theta = 172^\circ$ and (G) group of data for l_1, l_2, l_3 , and two displacements from d_a, d_b , and d_c). It is clear from these plots that M-tensor ratios show a considerable amount of nonlinear variation with

Table 2. Ratios of M-tensor component of ^{23}Na in NaNO_2 (including Na atom displacive nature) the numbers 1, 2 and 3 correspond to x -, y - and z -respectively

M-tensor ratios		M_{1111}/M_{3333}	M_{1133}/M_{3333}	M_{2323}/M_{3333}	M_{3131}/M_{3333}	M_{1212}/M_{3333}
Experimental values [19]	235 K	0.79	-0.73	0.05	0.16	0.11
	298 K	0.74	-0.68	0.06	0.16	0.13
	350 K	0.70	-0.63	0.08	0.20	0.16
Theoretical values	I	1.1	-0.87	0.12	0.58	0.3
	II	0.89	-0.79	0.06	0.6	0.23
	III	0.47	-0.67	0.03	0.04	0.07
	IV	1.01	-0.86	0.12	0.28	0.27
	V	0.74	-0.73	0.09	0.34	0.18
	VI	0.71	-0.74	0.07	0.17	0.17

Note: I ($\theta; l_1, l_2, l_3; d_c, d_a, d_b$) $\rightarrow$ ($180^\circ; 0.994, 0.078, 0.0767; 0.012 \text{ nm}, -0.049 \text{ nm}, 0.044 \text{ nm}$);

II ($\theta; l_1, l_2, l_3; d_c, d_a, d_b$) $\rightarrow$ ($176^\circ; 0.99, 0.11, 0.0883; 0.008 \text{ nm}, -0.034 \text{ nm}, 0.038 \text{ nm}$);

III ($\theta; l_1, l_2, l_3; d_c, d_a, d_b$) $\rightarrow$ ($178^\circ; 1, 0, 0; 0.013 \text{ nm}, -0.048 \text{ nm}, 0.042 \text{ nm}$);

IV ($\theta; l_1, l_2, l_3; d_c, d_a, d_b$) $\rightarrow$ ($182^\circ; 0.996, 0.075, 0.0486; 0.015 \text{ nm}, -0.046 \text{ nm}, 0.048 \text{ nm}$);

V ($\theta; l_1, l_2, l_3; d_c, d_a, d_b$) $\rightarrow$ ($167^\circ; 0.994, 0.078, 0.0767; 0.012 \text{ nm}, -0.049 \text{ nm}, 0.044 \text{ nm}$);

VI ($\theta; l_1, l_2, l_3; d_c, d_a, d_b$) $\rightarrow$ ($172^\circ; 0.996, 0.075, 0.0486; 0.015 \text{ nm}, -0.046 \text{ nm}, 0.048 \text{ nm}$)

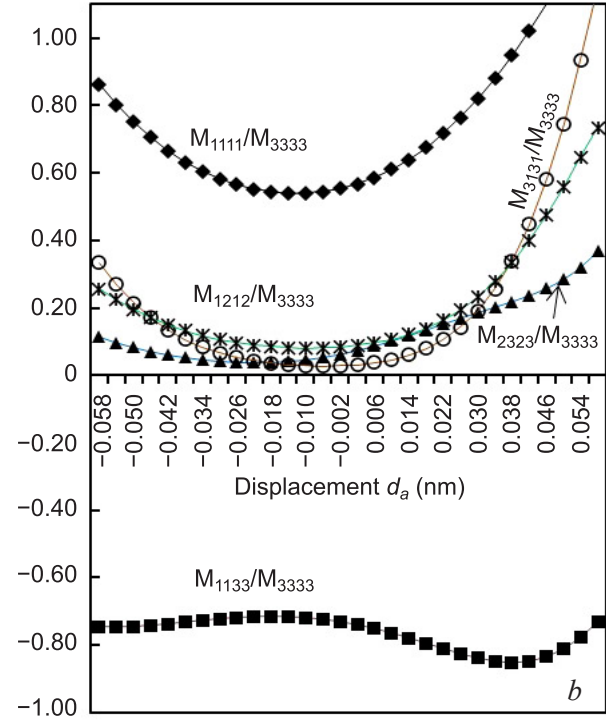
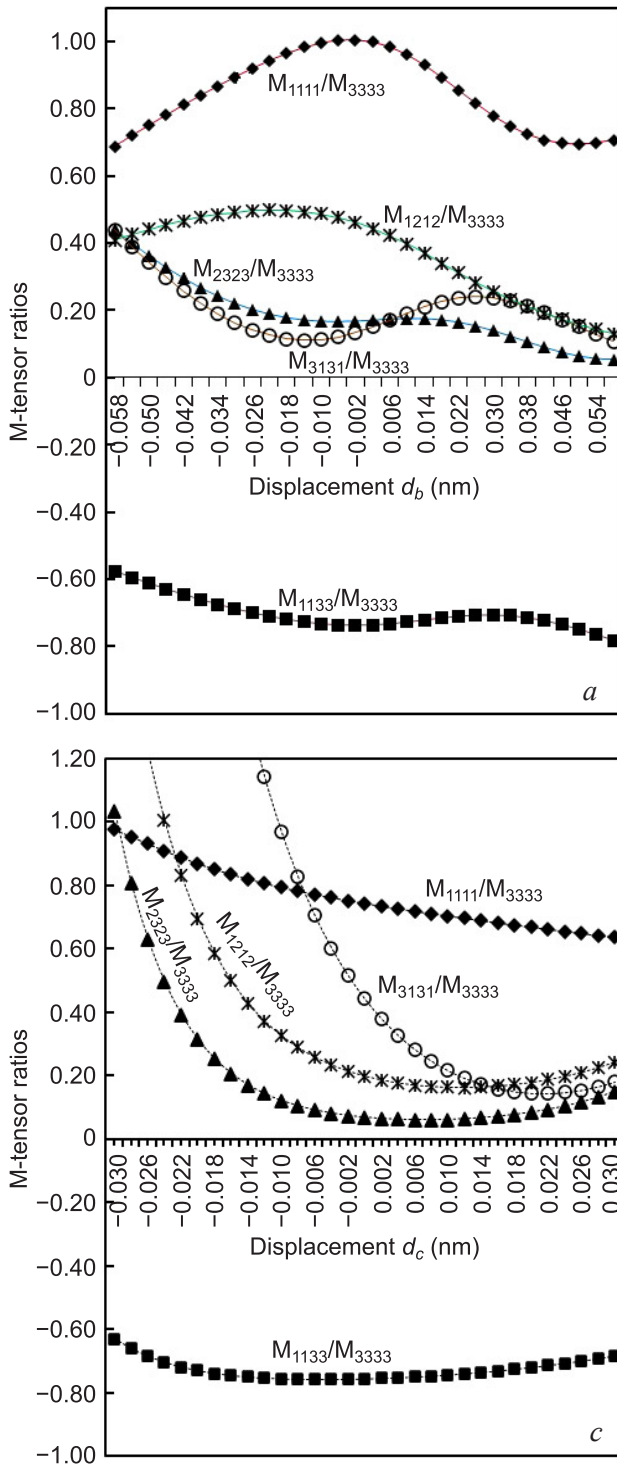


Figure 3. (a) M-tensor ratios as a function of b -axis displacement of Na atom at $T = 298$ K, the graph plotted for fixed value of other parameter flipping angle 172° , direction cosines of flipping direction $l_1 = 0.996$, $l_2 = 0.075$, $l_3 = 0.0486$; $d_a = -0.045$ nm, $d_c = 0.015$ nm; (b) M-tensor ratios as a function of a -axis displacement of Na atom at $T = 298$ K, the graph plotted for fixed value of other parameter flipping angle 172° , direction cosines of flipping $l_1 = 0.996$, $l_2 = 0.075$, $l_3 = 0.0486$; $d_b = 0.048$ nm, $d_c = 0.015$ nm; (c) M-tensor ratios as a function of c -axis displacement of Na atom at $T = 298$ K, the graph plotted for fixed value of other parameter flipping angle 172° , direction cosines of flipping $l_1 = 0.996$, $l_2 = 0.075$, $l_3 = 0.0486$; $d_b = 0.048$ nm, $d_a = -0.046$ nm

displacements d_a , d_b , and d_c . And it also shows the best match with the (G) group of data. This result confirms the displacive motion of the Na-atom during the sudden reorientation of NO_2 groups during the phase transition in NaNO_2 .

From Fig. 4a which is a plot of M-tensor ratios as a function of angle θ for different group of variables, it is clear that all M-tensors ratios are slowly varying functions of flipping angle θ ; the ratio M_{1133}/M_{3333} increases in negative higher values and rest all other four ratios increase in positive higher values and better

shows correspondences with experimental data at 172° . The variation of M-tensor ratios with angle of flipping is approximately exponential. Significant variations accounted for higher values of angle. Ratios M_{1111}/M_{3333} and M_{1133}/M_{3333} show larger variation than rest of three M-tensor ratios.

These results confirm that the quadrupole interactions of quadrupolar nuclei ^{23}Na with fluctuating external electric field due to dynamical flipping motions of NO_2 was largely affected along crystalline c -directions, hence larger change occurs in e.f.g.'s along this direction.

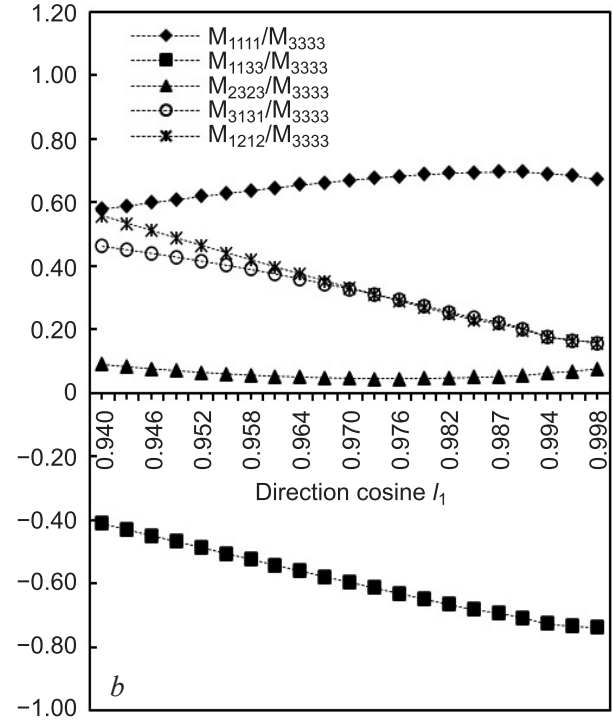
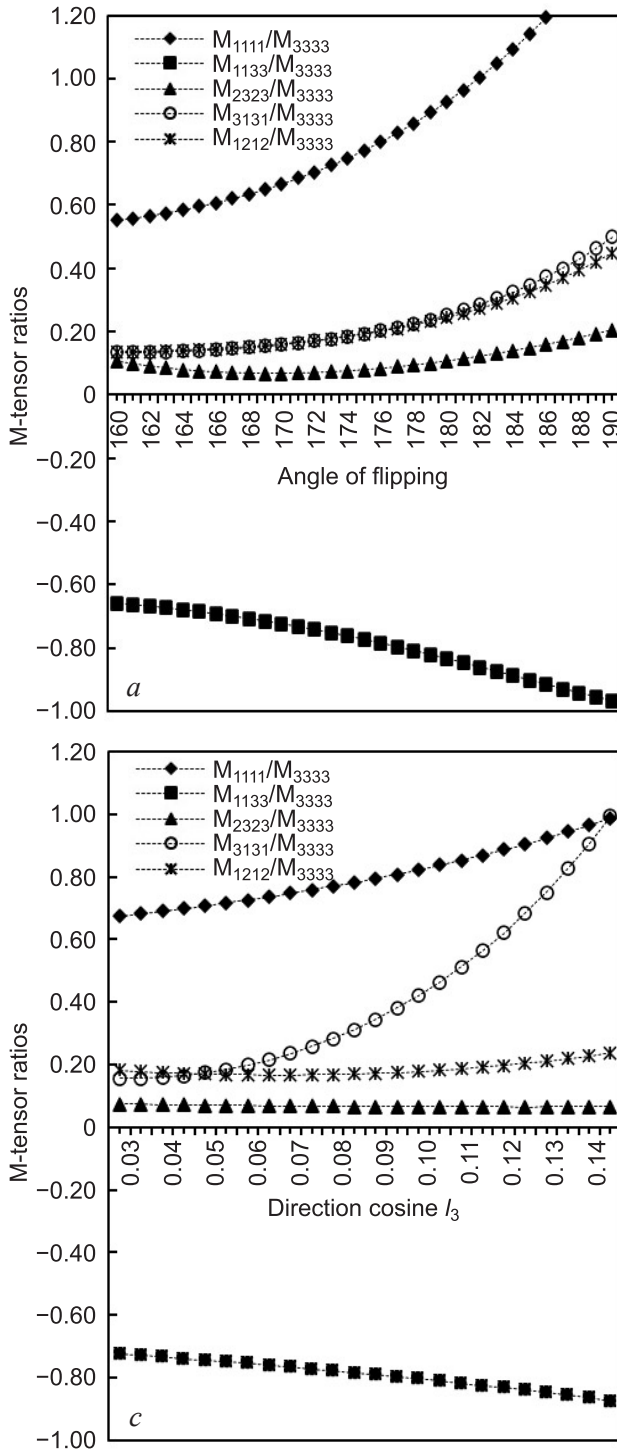


Figure 4. (a) M-tensor ratios as a function of flipping angle of NO₂ groups at $T = 298$ K here flipping direction taking nearest to crystalline c -axis. the graph plotted for fixed value of other parameter direction cosine of flipping $l_1 = 0.996$, $l_2 = 0.075$, $l_3 = 0.0486$; and displaced position co-ordinate of Na atom from old position is ($d_c = 0.015$ nm, $d_a = -0.046$ nm, $d_b = 0.048$ nm), (b) M-tensor ratios as a function of flipping direction cosine l_1 of NO₂ groups with flipping angle 172° at $T = 298$ K for fixed other parameter $l_3 = 0.0486$; and displacement of Na atom from old position along c -, a -, b -crystalline axis are 0.015 nm, -0.046 nm, 0.048 nm, (c) M-tensor ratios as a function of flipping direction cosine l_3 of NO₂ groups with flipping angle 172° at $T = 298$ K for fixed other parameter $l_2 = 0.075$; and displacement of Na atom from old position along c -, a -, b -crystalline axis are 0.015 nm, -0.046 nm, 0.048 nm

Figures 4b and 4c represent the plot for M-tensor ratios as a function of direction cosines l_1 and l_3 of flipping axis for fixed angle $\theta = 172^\circ$ and sodium ion displacements $d_a = -0.046$ nm, $d_b = 0.048$ nm, $d_c = 0.015$ nm. The variation of ratio M_{2323}/M_{3333} is found negligible but other ratios show considerable non-linear variations. From these plots we conclude that direction of rotation axis of NO₂ groups is neither a -axis nor c -axis as assumed in previous studies but it is fixed in space nearest to c -axis specified by direction cosines 0.996, 0.075, and 0.0486.

Table 2 represents the theoretical and experimental M-tensor data for various groups of parameters.

Conclusion

From our theoretical results following conclusion regarding the dynamical properties and local motions in NaNO₂ based on NMR experimental data are drawn:

1. NaNO₂ molecules possesses displacive ferroelectric nature with coordination of order-disorder nature of polarization reversal due to NO₂ groups i.e. its ferroelectric properties arise not only due to polarization reversal mechanism but also due to displacive behavior of Na ions, such displacement was produced due to thermal

fluctuation driven by soft phonon mode and fluctuating electric field gradients experienced by the sodium nuclei. Our analysis suggests a larger displacement (due to soft phonons and fluctuating electric field) of the Na atom which is due to Na atom gaining more thermal energy as T approaches T_c , this temperature change, brings soft phonons in action which amplifies thermal fluctuations leading to large-amplitude displacement of Na ions during phase transition. Na ion becomes more susceptible to thermal fluctuations and its restoring force is also reduced, which makes it easier for thermal energy to drive large-amplitude displacement of Na ions during the phase transition [31]. Hence sodium nitrite is not purely order-disorder type ferroelectric material.

2. At temperature 298 K near to room temperature during phase transition NO_2 groups flipped at 172° about an axis specified by direction cosines 0.996, 0.075, 0.0486 and Na- ion shifted at the position in space by an amount $d_c = 0.015$ nm, $d_a = -0.046$ nm, $d_b = 0.048$ nm along crystalline co-ordinate axes c , a , b respectively. This is entirely a new result which explains real dynamical local motions in NaNO_2 .

3. This work supports the concept of electric polarization having a spiral orientation of NO_2 groups in NaNO_2 [29]. In the theoretical analysis presented by us, the flipping angle of the NO_2 group is proved to be 172° and the flipping direction is specified by the direction cosines of 0.996, 0.075, and 0.0486. It is important to note here that the flipping direction does not correspond to the crystalline c -, a -, or b -axes, but lies in the crystalline space. These results clearly support the fact that the tip of electric polarization follows a spiral path due to the reorientation of NO_2 group during the phase transition. Hence, our work supports the concept of electric polarization with spiral orientation of NO_2 groups in NaNO_2 presented by D.G. Hughes and L. Pandey [31]. It also helps to explain the previous contradictions about the actual dynamic local motions in NaNO_2 ferroelectric. Previous works have not predicted considerable displacive character of Na ion in NaNO_2 and it was assumed order-disorder type ferroelectric material. Using this analysis, we can explain dynamical properties and internal motions in all other ferroelectric materials.

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